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Evaluation of Hygroscopicity Kinetic of Paper, Moulded Fibre Products and other Pore Materials

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Introduction

The hygroscopicity characterizes and belongs to very important behaviour of paper and paper products. On the one hand the hygroscopicity causes advantage of paper products, on the other hand causes some discrepancies of paper quality. These discrepancies hold down application of paper products. The complete understanding of humidification process is necessary presumption for further paper expanse utilization. Hygroscopicity of paper mass is very important behaviour especially for using of paper as packaging material.

The importance of underwritten tests is the examination of moulded fibre products behaviour at real condition in order to obtain a survey of humidification process during products storage. In appearances of customer requirements, it has been observed mostly a paper humidification at relative humidity of 75 % and 97 %. These relative humidity (R.H.) has been checked to simulate storage hall conditions partially ventilated and unventilated. Relative humidity of air alternates during product storage, i.e. after dosing the commodity into package. The commodities are frequently moist. For instance, in the case of egg tray, weight of egg decreases during 3 – 12 hours after lay (formation of air lock). The decrement is water. The water pass out to gas form or liquid and it is dependent on pressure and temperature during storage. A product with defined fibre compounds was selected for testing.

The water hold's ability of paper material from surrounding air humidity is notorious. The amounts of received water and velocity of this process is dependent on a lot of factors. Except temperature, pressure and relative humidity of air vicinity, the parameters as fibre components, degree of fibre beating, composition and amount of further fillers, degree of sizing and other auxiliary paper agents presence are important too. The most important property is porosity of paper material. Summarising we can say, that hygroscopicity of paper material is dependent on both the porosity and the surface-molecular properties of paper material.

Recently⁴ we have described the kinetic of paper and moulded fibre products humidification from start to equilibrium by following empirical equation (MMF) /1/:

$$y = (ab + cx^d) / (b + x^d) \quad /1/$$

where:

- **y** increment of sample moisture (w/w); $y = y_s - y_0$, y_s - real moisture, y_0 – moisture of sample at start of experiment;
- **x** time (in days) of sample storage at given R.H.;
- **d** characterises the rate of steady state adjustment;
- **c** characterises a hygroscopicity of porous materials.

Very useful is formulation of the time needed to achievement 90% or 99% of steady state moisture of paper mass sample, $T_{0,9}$ and $T_{0,99}$ /day/.

$$T_{0,9} = (9*b)^{1/d}$$

$$T_{0,99} = (99*b)^{1/d} .$$

Steady state moisture $y_r = c + y_0$ and relationship $v_h^0 = c/(1+b)$ are indicators of hygroscopicity and humidity rate at the start of humidification process of porous material, e.g. paper matter, respectively.

While steady state moisture of pore sample, $y_r = c + y_0$ has thermodynamically importance, the humidity rate at the start of humidification of pore sample $v_h^0 = c/(1+b)$ /day⁻¹/ characterises a kinetic of this process.

The value of steady state moisture of paper matter $y_r = c + y_0$ (rel. amount of water in porous paper medium w/w or %) in eq. /1/ characterizes a thermodynamic of the hygroscopicity, i.e. a fraction (w/w) of pores being occupied by condensed water⁴

$$y_r = \varepsilon_r \cdot 100 / [(OH/\rho_p) \cdot (\rho_p / \rho_v) + \varepsilon_r] .$$

ε_r – wet porosity, i.e. volume capacity of pores (dimensions: $0 < r \leq r(\varphi_{rel})$) filled with water at given R.H. = φ_{rel} .

$$\varepsilon_r = [OH/\rho_v] * [y_r/(100-y_r)], \quad /2/$$

where:

- ρ_v density of water (g/cm³);
- **OH** partially density of paper mass is expressed by relation basic weight of paper sample divided by thickness of sample (g/cm³);
- ρ_p density of solid part of cellulosic material³ = 1,56 g/cm³ ;
- φ_{rel} relative humidity (R.H.) of air.

The value of maximal equivalent cylindrical pore radius, $r(\varphi_{rel})$, being occupied yet by condensed water in pore material at R.H. = φ_{rel} and $T = \text{constancy}$ is then ensued from well-known Kelvin's equation /3/ (see e.g. Milichovský^{1,2})

$$r(\varphi_{rel}) = [(M*2*\gamma_{l,g}*\cos \theta) / (\rho_v * RT)] / \ln(1/\varphi_{rel}), \quad /3/$$

where:

- **M** molecular weight of water = 18;
- **T** temperature (K) ;
- **θ** contact angle between surface of capillary tube and meniscus of water inside characterises its shape - (in the case of full wetting is usually this angle equal to 0° and expression $(\gamma_{l,g} * \cos \theta)$ is equal to surface tension of water $\gamma_{l,g}$ (72,2.10⁻³ N/m at $T = 295$ K);
- **R** so called gas constancy (8,314 J.K⁻¹.mol⁻¹);

- $r(\varphi_{rel})$ radius of equivalent cylindrical pore (m).
The value of humidity rate at the start of humidification process

$$v_h^0 = c/(1+b) \text{ (rel. water amount in sample (w of water/w of sample)/time, i.e. day}^{-1}\text{)}$$

characterizes a kinetic of hygroscopicity process. This equation was received by linearization of eq. /1/ at start of humidification process being assumed $a \rightarrow 0$, i.e. by straight line through points of $x = 0, y = 0$ and $x = 1, y = c/(1+b)$. Both parameters, y_r and v_h^0 are important but parameter v_h^0 especially attract our attention, because enable us to evaluate the structure and surface-molecular properties of porous materials as e.g. paper and fibre moulded products.

Theoretical principles

Kinetic of pore material humidification at start of this process is characterised by following assumptions.

Assumption in $x = 0$ at temperature $T = \text{const.}$

1. The dry matter of pore material is relative high, i.e. the condensed water is filled the all smallest pores with equivalent cylindrical pore radius $r \leq r_{min}$.
2. The water condensation in pore material takes places predominantly through its surface pore layers.
3. At start of pore material humidification process, an influence of depth of surface layers on kinetic of this one is neglected (see assumption No.2).
4. The water condensation takes places only within surface layers of porous material.
5. The pore distribution is the same in all layers of pore material, i.e. it is equal to pore distribution of outer layers of pore material.

Moisture of pore material is given by water having been condensed in all of small pores $r \leq r_{min}$, where r_{min} is radius of maximal equivalent cylindrical pore being occupied by condensed water at start of humidification process. All humidity rate at start of pore material humidification process, v_h^0 is then given by following equation /4/, because the partial humidity rates at start of humidification process are different for every pore size group with equivalent pore radius of cylindrical pore ($r ; r+dr$).

$$v_h^0 = c/(1+b) = \int_{r_{min}}^{r(\varphi_{rel})} dv_h^0 \quad |4|$$

The value of infinitesimal addition of humidity rate at the start of humidification, dv_h^0 , is then proportional:

- to a drafting force of humidification process, F_h , which is changed during all this process, i.e. with increasing of paper moisture F_h decreases, and
 - to relative change of water concentration (w/w) in porous material $(\rho_l/OH) \cdot d\varepsilon$.
- With increasing seize of pores filled with condensed water the drafting force of humidification process, F_h will be decreased (see below).

$$dv_h^0 \approx (\rho_l/OH) \cdot dF_h, \quad |5|$$

where $d\mathbf{F}_h = \mathbf{p} \cdot \mathbf{A} \cdot d\boldsymbol{\varepsilon}$, because $d\mathbf{A}_f = \mathbf{A} \cdot d\boldsymbol{\varepsilon}$.

\mathbf{A} - outer surface of pore sample given by its geometry (m^2);

\mathbf{A}_f - free outer surface of pore sample (m^2); $\mathbf{A}_f = \mathbf{A} \cdot \boldsymbol{\varepsilon}$;

$\boldsymbol{\varepsilon}$ - all porosity of pore sample (V/V); $\boldsymbol{\varepsilon} = \mathbf{1} - \mathbf{OH}/\rho_p$ (e.g. see Skalický³);

ρ_l - liquid density, i.e. water density, ρ_v (g/cm^3).

Symbol \mathbf{p} denominates a pressure which is pressuring the vapour into pores to condensate.

The value of \mathbf{p} ensues from general Kelvin's equation (see Milichovsky⁵)

$$\frac{\rho_l \cdot RT}{M} \cdot \ln\left(\frac{p_\infty}{p_r}\right) = \frac{2\gamma_{l,g} \cdot \cos\theta}{r} + p, \quad |6|$$

where $\left(\frac{p_\infty}{p_r}\right) = \frac{1}{\varphi_{rel}}$ and p is an outer pressure..

The value of \mathbf{p} express an outer pressure on liquid within pore tubes having positive or negative value if this one decreases or increases a vapour tension, \mathbf{p}_r of the liquid contained in pores with equivalent pore radius of cylindrical pore (\mathbf{r} ; $\mathbf{r}+d\mathbf{r}$) relative to a vapour tension, \mathbf{p}_∞ , upon non-curved meniscus with $\theta = 0^\circ$, respectively. In the other words, providing that we put a cylindrical capillary of radius, \mathbf{r} , filled with water having meniscus shape characterised by contact angel, θ , and vapour tension about it, \mathbf{p}_r , at constant temperature in atmosphere with R.H. = φ_{rel} , than \mathbf{p} represents an outer pressure defined as

$$\mathbf{p} = -2 \cdot (\gamma_{l,g} \cdot \cos\theta) / \mathbf{r}$$

by which effective action we are able to achieve the vapour tension above water level closed within capillary, $\mathbf{p}_r = \mathbf{p}_\infty$ and vice versa. The pressure drafting vapour into pores with equivalent pore radius of cylindrical pore (\mathbf{r} ; $\mathbf{r}+d\mathbf{r}$) to condensate is so given by equation /7/.

$$\mathbf{p} = 2 \cdot (\gamma_{l,g} \cdot \cos\theta) / \mathbf{r} \quad /7/$$

By connecting of equations /5/ and /4/ with further additional correction by using of equation /7/ we received equation /8/ in following form.

$$v_h^o = c / (1 + b) \approx \frac{2 \cdot A \cdot \rho_l \cdot (\gamma_{l,g} \cdot \cos\theta)}{OH} \cdot \int_{r_{min}}^{r(\varphi_{rel})} \frac{\boldsymbol{\varepsilon}(r)}{r} dr \quad |8|$$

$$v_h^o = c / (1 + b) \approx \Pi_{g-c} \cdot \Pi_{s-m} \cdot \Pi_{str},$$

where Π_{g-c} is geometrical and concentration factor of porous material

$$\Pi_{g-c} = \frac{2 \cdot A \cdot \rho_l}{OH} ;$$

Π_{s-m} is surface-molecular factor

$$\Pi_{s-m} = (\gamma_{l,g} \cdot \cos \theta) ; \quad \text{and}$$

Π_{str} is structural factor characterizes pore structure of porous material.

$$\Pi_{str} = \int_{r_{min}}^{r(\varphi_{rel})} \frac{\varepsilon'(r)}{r} dr .$$

The equation /8/ describes then a hygroscopicity kinetic at start of pore material humidification process when only pores of equivalent cylindrical pore radius $r \leq r_{min}$ are filled with condensed liquid. Symbol $r(\varphi_{rel})$ is radius of maximal equivalent cylindrical pore being occupied by condensed water at equilibrium of humidification process having proceeded at air R.H. = φ_{rel} . All humidity rate at start of pore material humidification process, v_h^0 , is a composed function of three independent factors Π_{g-c} , Π_{s-m} and Π_{str} characterizing geometry and porosity of porous material, its surface-molecular and structural properties, respectively.

Surface-molecular properties of porous material

At natural condition, if no outer pressure influences exists, then factor $\Pi_{s-m} = (\gamma_{l,g} \cdot \cos \theta)$ characterizes a surface-molecular properties of the walls of porous material, because adhesion tension, σ_T , controlling capillary liquid phenomenon's, i.e. capillary elevation or depression, is given by equation /9/ (see Milichovsky⁵)

$$\sigma_T = \gamma_{l,g} \cdot f(\theta) , \quad /9/$$

where $f(\theta) = (1 - \sin \theta) / \cos \theta$ or $f(\theta) = [1 - \sin(\arccos \theta)] / \cos \theta$.

The value θ represents contact angle of liquid meniscus with pore wall.

Structural properties of porous material

Structure of porous material is described by structural factor Π_{str} . The function $\varepsilon'(r)$ in this factor represents the probability function of volume pore distribution of porous material defined as

$$\varepsilon'(r) = \frac{d\varepsilon}{dr} .$$

It is further stated that

$$\varepsilon_r = \int_0^{r(\varphi_{rel})} \varepsilon' .dr; \quad \varepsilon = \int_0^{\infty} \varepsilon' .dr; \quad \Delta\varepsilon_r = \int_{r_{min}}^{r(\varphi_{rel})} \varepsilon' .dr ;$$

where for $\mathbf{r}_{min} \rightarrow \mathbf{0}$ or $\mathbf{r}(\varphi_{rel}) \gg \mathbf{r}_{min}$ is $\Delta\varepsilon_r \rightarrow \varepsilon_r$. Supposing porous material composed of equivalent cylindrical pores with radius, \mathbf{r} , mean effective length, \mathbf{h} , and with \mathbf{N} of these pores in volume unit of porous material then we can described function ε' by following equation /10/

$$\varepsilon' = 2\pi.\mathbf{h}.\mathbf{r}.\mathbf{f}(\mathbf{r}).\mathbf{N} , \quad (10)$$

where $\mathbf{f}(\mathbf{r})$ is numerical probability function of pore distribution. By use of usual statistical function and the equation /10/, this case of pore distribution we can described as

$$\varepsilon = \pi.\mathbf{h}.\mu^2.\mathbf{N}, \quad (11a)$$

$$\varepsilon_r = \pi.\mathbf{h}.\mathbf{r}_r^2.\mathbf{N}_r = \pi.\mathbf{h}.\mathbf{r}_r^2.\mathbf{N}.\mathbf{F}_r(\mathbf{r}) = \varepsilon. \mathbf{F}_r(\mathbf{r}) .\mathbf{r}_r^2 / \mu^2 , \quad (11b)$$

$$\Delta\varepsilon_r = \pi.\mathbf{h}.\mathbf{r}_\Delta^2.\Delta\mathbf{N}_r = \pi.\mathbf{h}.\mathbf{r}_\Delta^2.\mathbf{N}.\Delta\mathbf{F}_r(\mathbf{r}) = \varepsilon. \Delta\mathbf{F}_r(\mathbf{r}) .\mathbf{r}_\Delta^2 / \mu^2 , \quad (11b)$$

where μ , \mathbf{r}_r and \mathbf{r}_Δ represented radius of arithmetic mean pore from all pore interval ($\mathbf{0} \leq \mathbf{r} \leq \mathbf{r}_{maxim}$), radius of arithmetic mean pore from pore interval ($\mathbf{0} \leq \mathbf{r} \leq \mathbf{r}(\varphi_{rel})$) and radius of arithmetic mean pore from pore interval ($\mathbf{r}_{min} \leq \mathbf{r} \leq \mathbf{r}(\varphi_{rel})$) of the porous material, respectively, because distribution functions $\mathbf{F}_r(\mathbf{r})$, $\Delta\mathbf{F}_r(\mathbf{r})$ and number of pores per volume unit of porous material \mathbf{N} , \mathbf{N}_r , $\Delta\mathbf{N}_r$ are defined as follows:

$$\mathbf{F}_r(\mathbf{r}) = \int_0^{r(\varphi_{rel})} \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad 1 = \int_0^{\infty} \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad \Delta\mathbf{F}_r(\mathbf{r}) = \int_{r_{min}}^{r(\varphi_{rel})} \mathbf{f}(\mathbf{r}).d\mathbf{r};$$

and

$$\mathbf{N}_r = \mathbf{N} . \int_0^{r(\varphi_{rel})} \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad \mathbf{N} = \mathbf{N} . \int_0^{\infty} \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad \Delta\mathbf{N}_r = \mathbf{N} . \int_{r_{min}}^{r(\varphi_{rel})} \mathbf{f}(\mathbf{r}).d\mathbf{r} .$$

The values of μ , \mathbf{r}_r and \mathbf{r}_Δ are then defined by following formulas.

$$\mathbf{r}_r . \mathbf{F}_r(\mathbf{r}) = \int_0^{r(\varphi_{rel})} \mathbf{r} . \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad \mu . 1 = \int_0^{\infty} \mathbf{r} . \mathbf{f}(\mathbf{r}).d\mathbf{r}; \quad \mathbf{r}_\Delta . \Delta\mathbf{F}_r(\mathbf{r}) = \int_{r_{min}}^{r(\varphi_{rel})} \mathbf{r} . \mathbf{f}(\mathbf{r}).d\mathbf{r} .$$

By connecting equations /10/, /11/ and /8/ with respect to the above mentioned conditions and rearranging all, we obtain equation /12/ in following form.

$$v_h^o \approx \frac{2.A.\rho_l.(\gamma_{l,g} \cdot \cos \theta)}{OH} \cdot \left(\frac{2}{r_\Delta^2} \right) . \Delta\varepsilon_r \quad /12/$$

Characterization of structural properties of porous material by parameter \mathbf{r}_Δ is not acceptable, because its value is changed with $\Delta\varepsilon_r$. If humidification interval of porous material at the

given conditions $\Delta\varepsilon_r \rightarrow \mathbf{d}\varepsilon$ then $\mathbf{r}_\Delta \rightarrow \mathbf{r}_r$ and in a case when $\Delta\varepsilon_r \rightarrow \varepsilon$ then $\mathbf{r}_\Delta \rightarrow \boldsymbol{\mu}$.
With respect to this fact, it is possible to describe this behaviour by following semiempirical function /13/

$$r_\Delta = r_{\min} + \frac{\boldsymbol{\mu} \cdot \boldsymbol{\omega} \cdot z}{(1 + \boldsymbol{\omega} \cdot z)}, \quad /13/$$

where $z = \Delta\varepsilon_r / (\varepsilon - \Delta\varepsilon_r)$.

The independent variable \mathbf{z} is relative pore concentration (V/V) filled with water, i.e. a volume ratio of pores filled with water at R.H. = φ_{rel} to volume of free pores.

Description of structural parameters

Parameters $\boldsymbol{\mu}$ and \mathbf{r}_{\min} represent the arithmetic mean value of pore radius and the minimal pore radius of porous material being occupied by condensed water at start of humidification process, respectively. The nondependent variable \mathbf{z} is changed in interval (0; ∞) and the independent variable is varied according to function /13/ in interval (\mathbf{r}_{\min} ; $\boldsymbol{\mu}$). This one means that parameter $\boldsymbol{\omega}$ characterizes compactness, i.e. negligible amount of biggest pores in porous sample and connectivity of numerical - represented by distribution $\mathbf{F}(\mathbf{r})$ or probability function $\mathbf{f}(\mathbf{r})$ - and volume - represented by distribution $\boldsymbol{\varepsilon}(\mathbf{r})$ or probability function $\boldsymbol{\varepsilon}'(\mathbf{r})$ - pore distribution of real porous material.

Notice:

As usually, with decreasing value of arithmetic mean pore radius, $\boldsymbol{\mu}$ a compactness of porous material increases and also the value of parameter $\boldsymbol{\omega}$ and vice versa. At comparable conditions, i.e. if compared samples of porous materials have approximately equally values of $\boldsymbol{\mu}$, an increasing value of parameter $\boldsymbol{\omega}$ indicates improving pore distribution characterised by more closely shape of this one and a better mono-dispersible character of pore distribution. A better shape similarity of volume and numerical pore distribution function is also this case, but as usually a really situation is characterised either by symmetrical $\mathbf{f}(\mathbf{r})$ and asymmetrical $\boldsymbol{\varepsilon}(\mathbf{r})$ or vice versa. If numerical probability function $\mathbf{f}(\mathbf{r})$ has usually symmetrical shape then a symmetry decrease of volume distribution with shift of its maximum relative to maximum of function $\mathbf{f}(\mathbf{r})$ to bigger values of \mathbf{r} is indicated by decrease of $\boldsymbol{\omega}$. In scarcely occurring opposite cases being indicated by increase of $\boldsymbol{\omega}$, if volume probability function has symmetrical shape and the numerical probability function $\mathbf{f}(\mathbf{r})$ is asymmetrical the markedly shift of its maximum relative to maximum of function $\boldsymbol{\varepsilon}(\mathbf{r})$ to smaller values of \mathbf{r} is observed.

Humidity rates v_h^0 - equation proposed for verification

By connecting equations /13/ and /12/ with appropriate mathematical rearranging, we received equation /14/ which is suitable for verification of experimental data, because ε_r and $\Delta\varepsilon_r$ are parameters measurable with very simple experimentally method.

$$v_h^0 = \left[\frac{(a_h \cdot \Delta\varepsilon_r^{0,5} + b_h \cdot \Delta\varepsilon_r^{1,5})}{(c_h + d_h \cdot \Delta\varepsilon_r)} \right]^2 = K \cdot f(\Delta\varepsilon_r), \quad /14/$$

where $\mathbf{a}_h = \boldsymbol{\varepsilon} \cdot \sqrt{\mathbf{K}}$; $\mathbf{K} = \mathbf{k}_h \cdot 4\mathbf{A} \cdot (\gamma_{l,g} \cdot \cos\theta) \cdot (\rho_l / \text{OH})$

$$b_h = (\omega - 1) \cdot \sqrt{K}$$

$$c_h = r_{\min} \cdot \varepsilon$$

$$d_h = (\mu + r_{\min}) \cdot \omega - r_{\min} .$$

The unknown parameters ω , μ and r_{\min} are describe above, parameter k_h is proportionality coefficient of general character ($\mu\text{m}^2 \cdot \text{m}^{-1} \cdot \text{mN}^{-1} \cdot \text{day}^{-1}$). The known parameter ε , is calculated by help of partial density of porous material **OH** (see eq. /5/). Structural and surface-molecular parameters are then calculated by use of the following equations /15/.

$$K = k_h \cdot 4A \cdot (\gamma_{1,g} \cdot \cos\theta) \cdot (\rho_1 / \text{OH}) = (a_h / \varepsilon)^2 \quad /15a/$$

$$\omega = (\varepsilon \cdot b_h / a_h) + 1 \quad /15b/$$

$$r_{\min} = c_h / \varepsilon \quad /15c/$$

$$\mu = [d_h - r_{\min} \cdot (\omega - 1)] / \omega \quad /15d/$$

Experimental works

The aim of experiments was to observe the humidity changes of porous samples at the given atmosphere with constancy relative humidity (R.H.). The achievement of paper and moulded fibre product's humidity was observed by using of gravimetrical method.

The sample of paper strip (dimension approximately 2*1 cm) was inserted in a glass weighting bottle of known weight. The contact of sample with wall of weighting bottle was minimal. Weighting bottle was airproofed and balanced. The sample of paper strip with exposed weighting bottle was put in desiccator in the following step. The desiccator was filled with prescribed solution of salts. This solution keeps a constant relative humidity in desiccator (see below). Before every balancing the weighting bottle was airproofed and in the next step the weighting bottle was took out from desiccator and balanced.

All experiments was taken place at room temperature 23 ± 1 °C.

The constant relative humidity in desiccator was achieved by use of saturated water solutions of these salts:

R.H. = 97%, solution of K_2SO_4

R.H. = 75%, solution of NaCl

R.H. = 49%, solution of KNO_2

Received data were then recalculated on moisture increment of sample (w/w, %) y (see equation /1/ or liter.⁴) and the dependence y vs. time of humidification x was made. Typical shape of these y vs. x curves is presented at Fig. 2. After verification of these dependences by use of kinetically model /1/ we received parameters: **a**, **b**, **c**, **d**, from which we calculated following characteristics (see equations /2/ and /3/):

- $v_h^0 = c / (1+b)$, humidity rate at the start of humidification process of porous material;
- the time needed to achievement 90% of steady state humidity of paper mass sample, $T_{0,9}$;
- steady state moisture $y_r = c + y_0$ of paper samples;
- the parameters $(\varepsilon_{97} - \varepsilon_{49}) / \varepsilon$ or $(\varepsilon_{97} - \varepsilon_{75}) / \varepsilon$ characterising extent of pore volume dispersion in porous material were calculated according to equation /2/ and /3/ (see liter.⁴) by use of φ_{rel} .

In order to evaluate structural properties of porous material by independent method, we have measured in suitable samples their volume pore distribution. In these cases the distribution of pores have been measured by pneumatical permeation method (see liter.^{3,6})

and characterised by median pore diameter, b_{50} and dispersity of pore distribution by pore difference parameter $\Delta b = b_{90} - b_{10}$. The method of determination of both parameters b_{50} and Δb is depicted in Fig. 1.

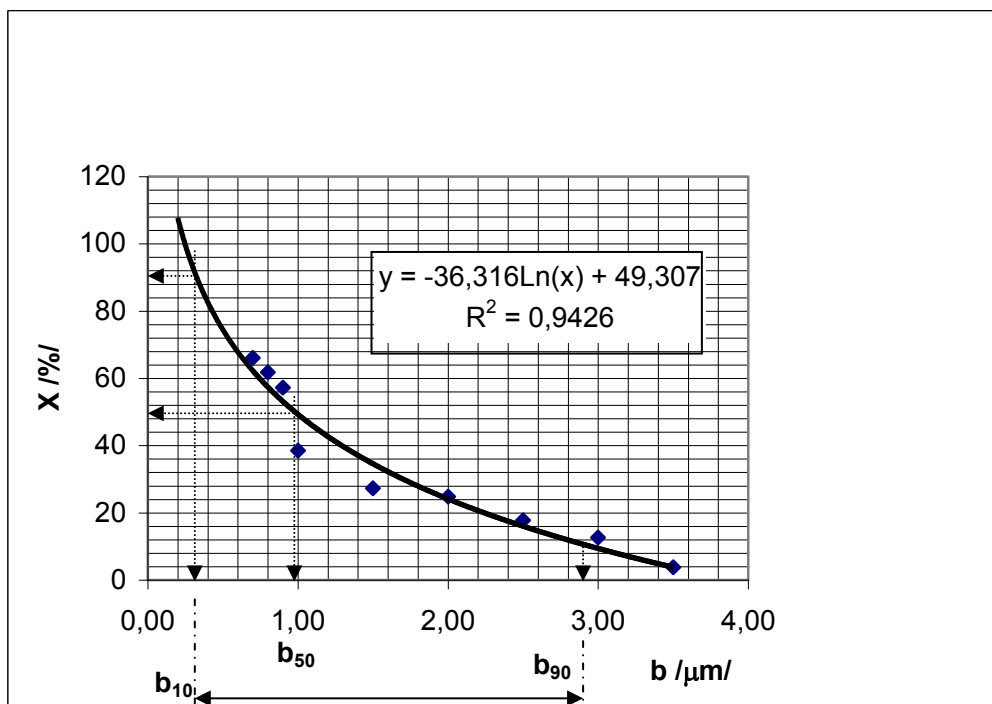
Used fibrous material

Formerly was examined currently used fibrous material in production of moulded fibre products (mostly mixture of groundwood and secondary pulp). This result has already been published (see Adámková⁴). In this study we used paper sheets and moulded fibre products manufactured at plant conditions and composed of the following fibrous components.

- C12 – a white sort of waste paper (classification EN 643)
- A10 – a worse sort of waste paper (classification EN 643)
- Grey – a mixture sort of waste paper
- Sulphate bleached pulp (softwood pulp, 68% White Spruce, 32% Lodgpole Pine, trace of Balsam Fir, NIST standard reference pulp 8495)
- Sulphate bleached pulp from Eucalyptus (hardwood pulp, NIST standard reference pulp 8494)
- Newsprint paper
- Groundwood, groundwood pulp from spruce

The items above formed then the pulp slurries from which paper products were prepared in flat or moulded form.

Fig. 1: Volume pore distribution for bleached sulphate softwood pulp sheet.



Degree of sizing was identified by drop method (see remark to Table II and III), because we disposed only in the case of moulded form by small pieces of flat samples.

Results and discussion

The humidity rate at the start of humidification process, $v_h^0 = c/(1+b)$ is a main parameter characterizing the kinetic of humidification process of porous material including paper matter. As expected, this parameter should be increased particularly with increase of R.H. as documented by Fig. 3. More exactly as resulted from equation /12/ or /14/, parameter v_h^0 increased nonlinearly with relative free pore volume potentially occupied with water, $\Delta\varepsilon_r$ at the given atmospherically condition, i.e. at R.H. = ϕ_{rel} (see Fig. 4).

It seems, that similar behaviour it is possible to expect in the case of further kinetic parameter $T_{0,9}$. The time needed to achievement 90 % of steady state moisture of paper mass sample, $T_{0,9}$ /day/, is also increasing with enhancing values of $\Delta\varepsilon_r$ as demonstrated by Fig. 5 but not at all observed cases.

According to these facts, data of humidity rate at the start of humidification process, $v_h^0 = c/(1+b)$ were further verified by use of equations /14/ and /15/ in order to obtain parameters full characterised structural (μ, ω) and surface-molecular (σ_T) properties of studied paper matters. Both the constancies a_h, b_h, c_h, d_h in equation /14/ as well as the parameters K, ω, r_{min}, μ having been resulted of these ones (see equation /15/) are then summarized for all searched paper materials in Table I.

The results of data evaluation from all humidification experiments are summarized in Tables II and III. All main results describing as surface-molecular properties so structural parameters of paper sheets and moulded fiber walls of different fiber composition, filled or no filled with mineral fillers, sized with synthetic sizing aids on AKD basis or not sized, are summarized in Table II. A comparison of structural properties identified by both the recently described humidification method⁴ extended by parameters μ and ω as described above and by classical pneumatical method is presented then in Table III.

Surface-molecular properties

For calculation of adhesion tension, σ_T characterising of surface-molecular properties of pore walls was utilised factor $\prod_{s-m} = (\gamma_{l,g} \cdot \cos\theta)$ (see Eq. /9/) expressed by parameter $K = (a_h/\varepsilon)^2$ in equation /15a/. All independent variables in this equation /15a/ except proportionality coefficient k_h are known. This process and material independent coefficient k_h was determined by help of standardised softwood bleached sulphate pulp sheet with known value of adhesion tension, σ_T being published for this sort of pulps in literature⁷ and measured by so called GRAP method (see below).

$V_h^0/f(\Delta\varepsilon_v) =$	919,2	(1/day)
A =	0,0042	(m ²)
$\sigma_T(\text{GRAP})=$	40	(mN/m)
cos θ =	0,847772	-
$\gamma_{l,g}$ =	72,2	(mN/m)
ρ_l =	998	(kg*m ⁻³)
$\gamma_{l,g} \cdot \cos\theta =$	61,21	(mN/m)
ρ_l/ρ_H =	1,373	-
k_h =	657,2575	($\mu\text{m}^2 \cdot \text{m}^{-1} \cdot \text{mN}^{-1} \cdot \text{day}^{-1}$)

As ensues from Table II as well as Table III, adhesive tension, σ_T , is very important parameter which is changed by chemical composition of pore surface. It is negligible changed by use of clean cellulosic material, more changed by use of lignocelulosic particularly high yield material, e.g. groundwood and other fillers but predominantly σ_T is changed by sizing of paper matter. The smallest value of σ_T achieved samples No. 5, 4, 8 and 3, i.e. the samples with highest degree of sizing (see Table II). Logically, provided that paper sizing is effective, an increasing of paper sizing is resulted in decrease a value of σ_T . The value of σ_T decreases with improving of hydrophobia of pore walls and vice versa.

Adhesion tension, σ_T forming the factor \prod_{s-m} , is very important parameter of humidification kinetic but only at beginning of humidification process. An influence upon time needed to achievement 90 % of moisture steady-state of paper mass, $T_{0,9}$, was not approved (see in detail Table II).

Structural properties

As described above in parts “Description of structural parameters” and „Experimental works”, the structural parameters of pore materials ensuing from humidification measurements are following:

μ – the arithmetic mean value of equivalent pore radius;

ω – the compactness of porous material;

$(\epsilon_{97}-\epsilon_{49})/\epsilon$ – the extent of pore volume dispersion in porous material with approximately equally mean values of their pore sizes.

Received results are also summarized in Tables II and III.

The results in Table III indicate logical difference in arithmetical mean value of numerical pore distribution, μ , and median pore radius, $b_{50}/2$, characterising the volume pore distribution. In all cases it was observed that μ is smaller then $b_{50}/2$. Both pore volume distribution characteristics describing of its dispersion by qualitatively different parameters, the extent of pore volume dispersion, $(\epsilon_{97}-\epsilon_{49})/\epsilon$, and the pore difference parameter, $\Delta b = b_{90} - b_{10}$, show equally trends. The most mono-dispersive character has sample No. 2 composed by 100% of bleached hardwood pulp controversially to the most poly-dispersive character of sample No. 11 composed by 50 % of groundwood. The sample with groundwood is also formed by bigger pores compared particularly with samples No.1 and No.2 composed by 100 % of chemical pulps.

It is logical that in mostly cases parameter ω should be increased with decreasing of mean pore radius, μ , because increasing the compactness of porous material as documented in Fig. 6. In this case the value of parameters ω in pulp sheet composed of bleached sulphate hardwood pulp from Eucalyptus (sample No.2) is 3,70 in comparison with pulp sheet composed of bleached sulphate softwood pulp (sample No.1) predominantly from pine ($\omega = 2,23$). With increasing value of parameter ω the influence of big pores on numerical pore distribution decreases, i.e. porous material has lesser and lesser amount of big pores and is more and more compact. As documented Table III, the highest compactness indicates sample No. 5 with smallest mean pore followed by samples No.6, 4 and 7. These samples are depicted with relatively high content of fillers as indicated by ash content. Samples with high amount of groundwood indicate the smallest compactness.

Influence of sizing on humidification process

The influence of paper sizing on paper humidification is predominantly in suppressing of surface activity of pore walls to water molecules quantitatively described by adhesion tension,

σ_T (see part “Surface-molecular properties”, compare also results in Table II and curves in Fig. 3). With regard to other important parameters of humidification process as described: $T_{0.9}$ - the time needed to achievement 90% of steady state moisture of paper mass and y_r - the steady state moisture of pore sample, it have not been proved any influence of sizing on these parameters (see Table III). Especially in the case of steady state moisture of paper samples, the shape and location of curves describing the dependence y_r vs. R.H. are practically equally regardless of composition and surface-molecular properties of porous materials as documented in Fig. 7.

However, the steady state moisture of pore sample, y_r , decreases with increasing value of partial density of paper as documented in Fig. 8, because, logically, with increasing of partial density of porous material ρ_H a free volume capacity determined by its porosity ϵ decreases.

Hygroscopicity influence on strength and mechanical properties of paper material

It is logical, that any properties closely connected with moisture content of paper and other porous material, e.g. strength and mechanical properties are typical, have to be influenced by this one. We have observed hygroscopicity influence on the strength and mechanical properties of paper material by stiffness measurement of this one. Stiffness is defined by rate of external force moment action and deformation displacement in Hook's linear extent of deformation measured at direction of force moment exerted on place of action.

Description of stiffness measurement

Stiffness⁸⁻¹¹ was determined by use of device TIRAtest 26005. Strip of dry sheet, with measured its thickness in mm (τ), have been used for measurement of these properties. The width of these strips were $b=20$ mm. A distance of support point L_V / was set up on 5 cm. The applied force acted in centre between them. The Scheme 1 shows a measuring part of appliance. Graphical depiction the course of test is shown in Scheme 2. The used software has evaluated a course of test automatically and further has been calculated following parameters:

RbH - bending strength (N/mm²);

$$RbH = (1.5 \cdot FH \cdot L_V) / (b \cdot \tau^2);$$

FH - supreme force (N);

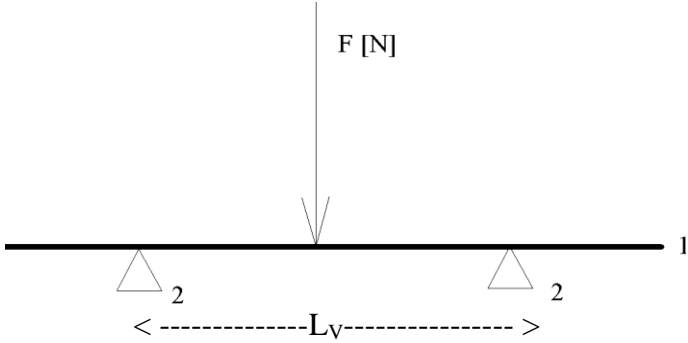
and deflection work, **I_p**, according to equation

$$I_p = \int_0^{\delta} 10^{-3} \cdot (F \cdot dx), \quad (J).$$

Stiffness was than calculated⁹⁻¹¹ as

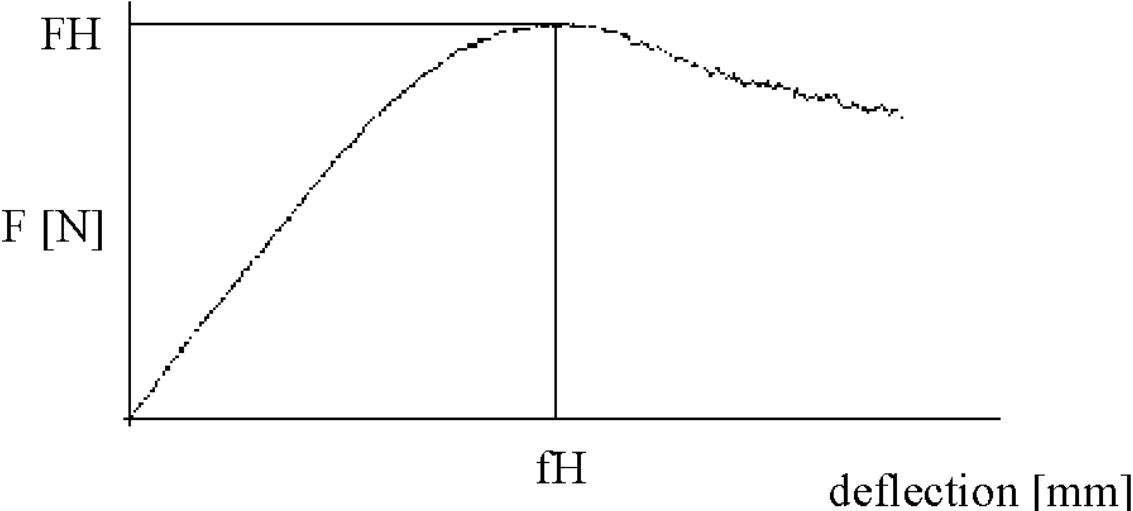
$$T = \frac{F \cdot L_v^3}{\delta \cdot b \cdot 48}$$

Scheme 1: Schematically depiction of stiffness measurement.



- 1 - tested sample,
- 2- two support point of sample strip

Scheme 2: Dependence of touch force to sample upon its deflection.



and Stiffness Index, **T** was then recalculated according to equation /16/ on the standard thickness τ_0 of specimen, $\tau_0 = 1\text{mm}$ (**T₀**), because

$$T_o = \frac{l}{b} \cdot E \cdot I = E \cdot \frac{\tau_o^3}{12} \quad (\text{N.mm}) \quad \text{and} \quad \frac{E}{12} = \frac{T}{\tau^3} \quad /16/$$

Symbols:

L_v - distance between support point (see Scheme 1), mm;

δ - deflection in linear part of a relationship $F=f(\text{deflection})$, mm;

b - width of specimen, mm;

τ - thickness of specimen, mm;

E - Young`s modulus, calculated for every measured thickness of specimen by help of equation /16/ (N/mm^2);

F - bending strength (see Scheme 1) corresponding deflection δ in linear part of a relationship $F = f(\text{deflection})$, N;

I - moment of inertia the cross-section of measured specimen with a width b and thickness τ (mm^4).

Determination of paper sheet-yielding

The ability of paper wall during its deflection to crumble followed occasionally by its destruction is very important the material quality, e.g. of mostly moulded fibre packaging. The main object of these measurements was to receive any information about this behaviour influenced by water.

Further important parameters receiving during stiffness measurements are:

FH_x - touch force to sample at its deflection x mm, N;

dFH_x - difference between the supreme force **FH** and **FH_x**, N

δFH_x - rel. difference $100 \cdot (\text{FH} - \text{FH}_x) / \text{FH}$, %.

All these parameters characterize the mechanical properties of paper sheets, i.e. a paper sheet-yielding - the ability of paper strip to crumble. With increasing of **dFH_x** or **δFH_x** the friability of paper sheet grows up as well and vice versa. The values of **dFH_x** or **δFH_x** are lower the paper sheet flexibility is better.

The all test measurements were carried out with samples having been acclimatised before each measurement 13 days in desiccator at R.H. = 50, 75 and 97 % and temperature $23 \pm 1^\circ \text{C}$. The received results are presented in Table IV.

Comment of received results

As expected, the better stiffness of dry paper strip - i.e. acclimatised at low R.H. and non acclimatised paper strip - was observed in the case of sample No. 11 composing of 50% groundwood compared with sample No. 12 being completely composed of secondary fibre, because the thickness of paper strip No. 12 was approximately half of paper strip No. 11. However, by recalculation into Stiffness Index, **T_o** – according to equation /16/ - the situation

is dramatically changed. Sample containing only secondary fibre has better Stiffness Index, T_o , because its partial density, OH is substantially higher.

By comparison both the sized (sample No. 11) and the non-sized (sample No. 12) paper strip, a deep influence of surface-molecular modification of pore walls on connectivity strength and mechanical properties with its hygroscopicity was observed but only at start of humidification process. However, this connectivity is strongly influenced by composition of paper material. We can see again dominant influence of the groundwood on friability of paper sheets (see Fig. 9).

As well known, water is acting in porous material as effective plasticizer but its influence is strongly affected by composition of paper matter. In the case of groundwood contained in sample No. 11, the both values dFH_{12} , dFH_{15} or δFH_{12} , δFH_{15} characterizing friability of paper sheets decrease dramatically with increase of R.H., i.e. friability of paper strip decreases with increase of R.H. more intensive then in the case of sample No. 12 composed only of secondary fibre (see Fig. 9).

Conclusion

Theoretical description and experimental verification of kinetic of paper humidification has been allowed for a better understanding to hygroscopicity behaviour of generally the all porosity materials including paper, wood, textiles synthetic and natural origin, building materials etc.

Mathematical description of this process enable us to provide not only qualitatively but also quantitatively control of humidification process. This is on the one hand. On the other hand it was shown, that a kinetic of paper humidification is controlled by surface-molecular and structural properties of porous material inclusive its geometry, i.e. its effective outer surface.

However, if both the surface-molecular and structural properties of porous material are effective at beginning of humidification process the amount and structure of pores only control a steady state of this process, i.e. moisture content of porous material. The effect of hydrophilic or hydrophobic character of pores is so effective only at beginning of humidification process.

Strength and mechanical properties being strongly connected with the moisture content of porous material, e.g. paper, are typically influenced by humidification process and with the rules following its behaviour, i.e. with its kinetic and thermodynamic.

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Tables:

Table I: Summarizing results of verification $v_h^0 = K.f(\Delta\varepsilon_r)$ dependencies according to equation /14/ and /15/.

Paper sheet's characterization	$\rho_l/0H$	A (m ²)	a_h	b_h	c_h	d_h	$v_h^0/f(\Delta\varepsilon_r) = K$	ω	r_{min} (μm)	μ (μm)	Composition of pulp slurry
Bleached softwood sulphate pulp - standard pulp [1]	1,373	0,0114	13,12	30,19	1,229	10,62	603,8	2,23	2,30	3,50	Primary fibre
Bleached hardwood sulphate pulp - standard Eucalyptus pulp [2]	1,165	0,0131	11,17	66,97	1,068	18,49	614,1	3,70	2,37	3,26	Primary fibre
Moulded form [Cat. starch + Parafinic disper.], [3]	3,243	0,0131	14,49	107,37	1,112	17,15	326,0	6,95	1,38	1,28	Secondary fibre, 14,1 % ash
Moulded form [Cat. starch + AKD size], [4]	3,221	0,0131	11,26	145,19	0,866	20,58	197,3	11,34	1,08	0,83	Secondary fibre, 12,5 % ash
Comparable moulded form [AKD size], [5]	3,356	0,0131	5,76	245,24	0,413	29,13	50,7	35,45	0,51	0,33	Secondary fibre, 14,1 % ash
Moulded form, sized, [6]	3,360	0,020	27,35	451,85	1,03	64,33	1141,2	14,38	1,27	3,30	Secondary fibre, sized, 15,3 % ash
Moulded form, unsized, [7]	3,349	0,020	27,79	249,20	1,82	33,42	1180,0	8,25	2,25	2,07	Secondary fibre, unsized, 12,5 % ash
Moulded form, sized, [8]	2,856	0,013	13,00	55,00	1,10	20,00	280,7	4,28	1,42	3,58	Secondary fibre, sized, 16,3 % ash
Moulded form, unsized, [9]	2,889	0,013	26,40	75,65	2,51	20,78	1149,4	3,23	3,22	4,20	Secondary fibre, unsized, 13,3 % ash
MF: 100%A10+AKD size+ Cat. starch [10]	3,070	0,0200	17,24	48,60	1,05	14,82	461,0	3,26	1,30	3,64	Secondary fibre A10 "bond", sized
MF: 50%groundwood+ 25% C12+ 25% grey+ AKD Sizer + Parafinic dispersion [11]	4,338	0,0090	19,35	45,93	1,51	14,70045	583,0	2,90	1,88	3,83	50%groundwod, 50% secondary fiber, sized
MF: 100% A 10 [12]	2,178	0,010	21,47	13,50	1,51	11,94590	703,4	1,51	1,87	7,29	Secondary fibre A10 "bond", unsized

Table II: Comparison of structural and surface-molecular properties of different paper sheets

Paper sheet's characterization	OH (kg/m ³)	ε	$(\varepsilon_{97}-\varepsilon_{49})/\varepsilon$ (%)	$y_r(\text{RH}=97\%)$ (%)	μ (μm)	ω	σ_T (mN/m)	$v_h^\circ(\Delta\varepsilon_r=0,1)$ (1/day)	$T_{0,9}(\Delta\varepsilon_r=0,1)$ (day)	Drop test* (s)	Composition of pulp slurry
Bleached softwood sulphate pulp - standard pulp [1]	727,0	0,5340	35,11	25,61	3,50	2,23	40,0	4,96	14	-	Primary fibre
Bleached hardwood sulphate pulp - standard Eucalyptus pulp [2]	857,0	0,4506	47,37	25,12	3,26	3,70	42,7	3,75	13	-	Primary fibre
Moulded form [Cat. starch + Parafinic disper.], [3]	307,7	0,8028	10,57	27,02	1,28	6,9	6,1	7,97	100	1482	Secondary fibre, 14,1 % ash
Moulded form [Cat. starch + AKD size], [4]	309,8	0,8014	9,92	25,91	0,83	11,3	3,7	7,77	105	2676	Secondary fibre, 12,5 % ash
Comparable moulded form [AKD size], [5]	297,4	0,8094	9,52	25,75	0,33	35,4	0,9	8,29	130	3180	Secondary fibre, 14,1 % ash
Moulded form, sized, [6]	297,0	0,8096	11,23	26,42	3,30	14,4	13,9	9,46	-	71,2	Secondary fibre, sized, 15,3 % ash
Moulded form, unsized, [7]	298,0	0,8090	10,37	25,29	2,07	8,3	14,4	10,43	-	0,2	Secondary fibre, unsized, 12,5 % ash
Moulded form, sized, [8]	349,5	0,776	11,53	24,47	3,58	4,3	5,9	3,56	140	1530	Secondary fibre, sized, 16,3 % ash
Moulded form, unsized, [9]	345,4	0,779	12,21	25,59	4,20	3,2	27,3	5,48	198	18	Secondary fibre, unsized, 13,3 % ash
MF:100%A10+AKD size+ Cat. starch [10]	325,0	0,7917	8,75	23,28	3,64	3,3	6,0	7,64	40	108	Secondary fibre A10 "bond", sized
MF:50%groundwood+ 25% C12+ 25% grey+ AKD Sized + Parafinic dispersion [11]	230,0	0,8526	8,32	29,19	3,83	2,9	12,1	6,45	42	940	50%groundwod, 50% secondary fiber,sized
MF: 100% A 10 [12]	458,0	0,7064	14,59	23,05	7,29	1,5	28,2	7,11	35	14,8	Secondary fibre A10 "bond",unsized

Drop method: time of full penetration of 0,06 ml distilled water into paper sheet; measured on smooth side of a paper sheet.

Table III: Structural properties of different paper sheets characterised by volume and numerical pore distribution

Paper sheet's characterization	OH (kg/m ³)	ϵ	$(\epsilon_{97}-\epsilon_{49})/\epsilon$ (%)	$y_r(\text{RH}=97\%)$ (%)	μ (μm)	ω	$b_{50}/2$ (μm)	$\Delta b=b_{90}-b_{10}$ (μm)	Drop test* (s)	σ_T (mN/m)	$v_h^{\circ}(\Delta\epsilon_v=0,1)$ (1/day)	Composition of pulp slurry
Bleached softwood sulphate pulp - standard pulp [1]	727,0	0,5340	35,11	25,61	3,50	2,23	0,50	2,7	-	40,0	4,96	Primary fibre
Bleached hardwood sulphate pulp - standard Eucalyptus pulp [2]	857,0	0,4506	47,37	25,12	3,26	3,70	0,11	1,6	-	42,7	3,75	Primary fibre
MF:50%groundwood+ 25% C12+ 25% grey+ AKD Size + Parafinic dispersion [11]	230,0	0,8526	8,32	29,19	3,83	2,90	1,25	11,5	940	12,1	6,45	50%groundwod, 50% secondary fiber,sized
MF: 100% A 10 [12]	458,0	0,7064	14,59	23,05	7,29	1,51	0,48	3,3	14,8	28,2	7,11	Secondary fibre A10 "bond",unsized

*Remark:

Drop method: time of full penetration of 0,06 ml distilled water into paper sheet; measured on smooth side of a paper sheet.

Table IV: Hygroscopicity influence on mechanical and strength properties of moulded fibre walls.

R.H.(%)	PH(g.m ⁻²)	OH(kg.m ⁻³)	Sample	τ (mm)	τ^3	F/ δ (N/mm)	FH(N)	FH ₁₂ (N)	FH ₁₅ (N)	dFH ₁₂ (N)	δ FH ₁₂ (%)	dFH ₁₅ (N)	δ FH ₁₅ (%)	I _p (J)	T(N.mm)	T ₀ (N.mm)	E(N/mm)
97	464	230	MF No. 11 50% groundwood	2,000	8,000	0,6288	1,443	1,334	1,254	0,109	7,56	0,189	13,07	0,00695	81,9	10,2	122,8
75				2,080	8,999	1,1650	2,572	2,233	2,029	0,339	13,18	0,543	21,12	0,01118	151,7	16,9	202,3
50				2,070	8,870	1,3082	3,081	2,525	2,300	0,556	18,05	0,781	25,35	0,01091	170,3	19,2	230,5
nonacc.				2,012	8,141	1,0937	2,695	2,270	2,075	0,425	15,77	0,620	23,01	0,01018	142,4	17,5	209,9
97	445	458	MF No. 12 A 10 unsized	0,970	0,913	0,1908	0,627	0,607	0,582	0,021	3,27	0,046	7,26	0,00451	24,8	27,2	326,7
75				0,980	0,941	0,2953	0,963	0,919	0,871	0,044	4,52	0,092	9,51	0,00613	38,5	40,9	490,3
50				0,950	0,857	0,3033	1,051	1,002	0,916	0,048	4,62	0,135	12,85	0,00620	39,5	46,1	552,8
nonacc.				0,973	0,920	0,2984	1,018	0,983	0,924	0,034	3,36	0,093	9,17	0,00570	38,9	42,2	506,9

Abbreviations:

nonacc. - non acclimatised

PH - grammage of paper sheet

OH - partial density of paper sheet

Figures:

Fig. 2 : Kinetic of moulded fibre walls humidification at 97 %, 75 % and 49 % R.H.

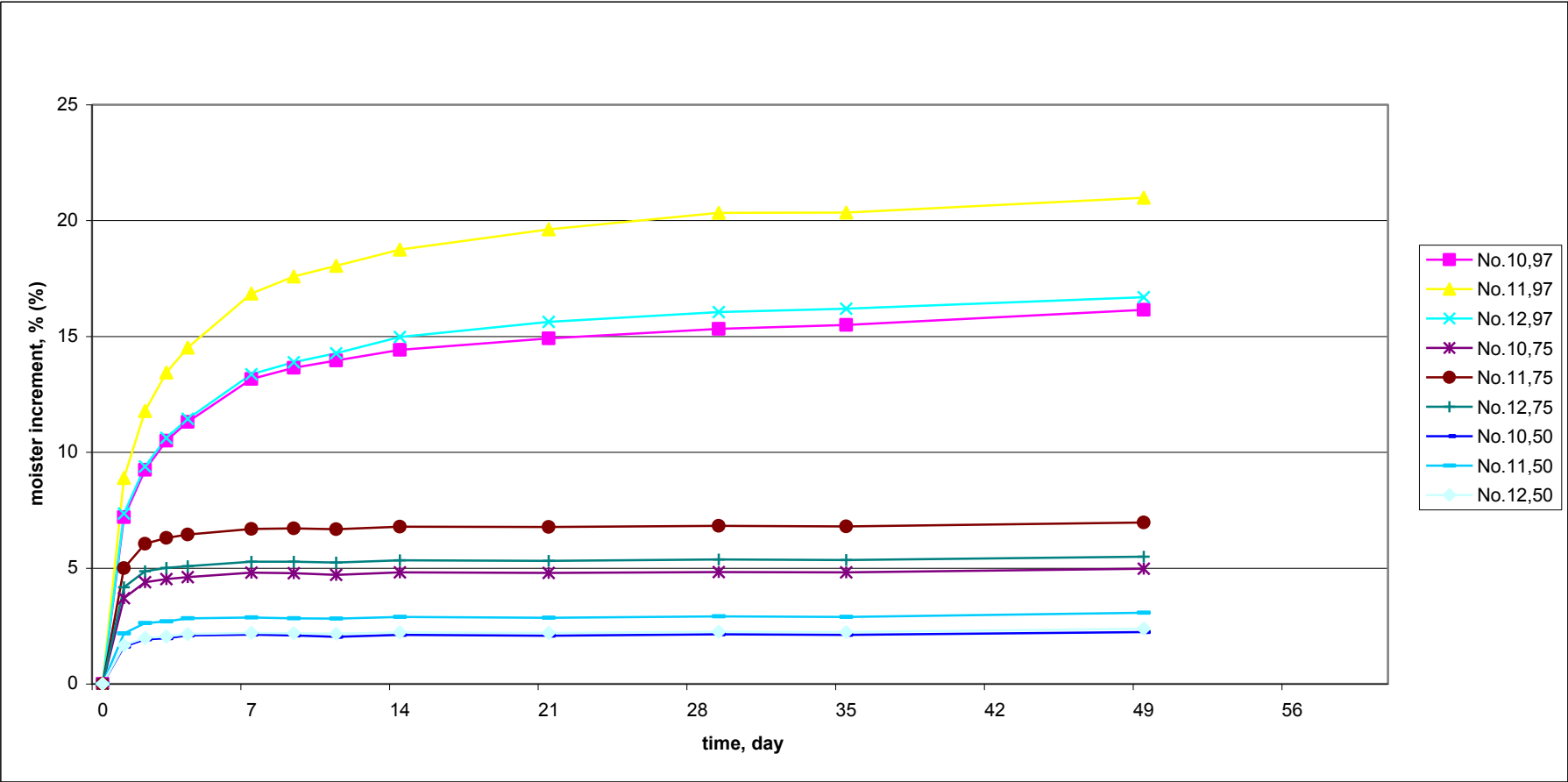


Fig 3. : Humidification rate at start of process vs. R.H.

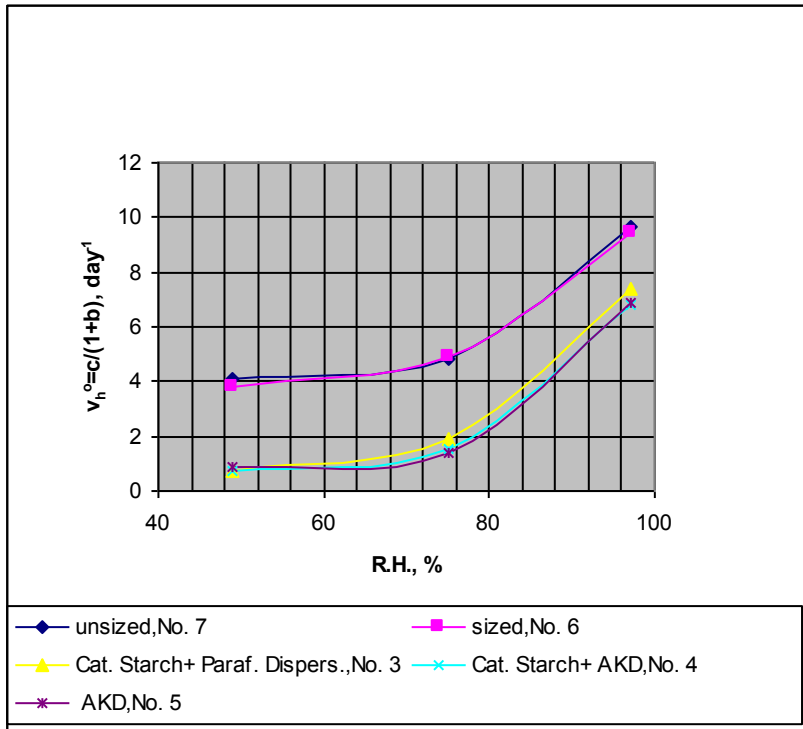


Fig. 4: Verification of surface-molecular properties -kinetic of paper humidification.

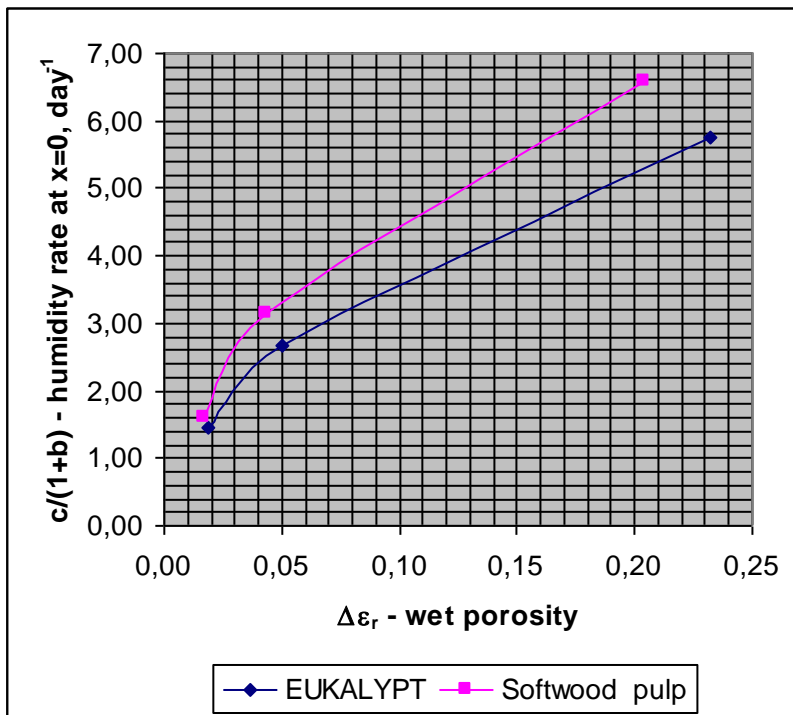


Fig. 5: Verification of kinetic of paper humidification - equilibrium time vs. wet porosity of pulp sheet.

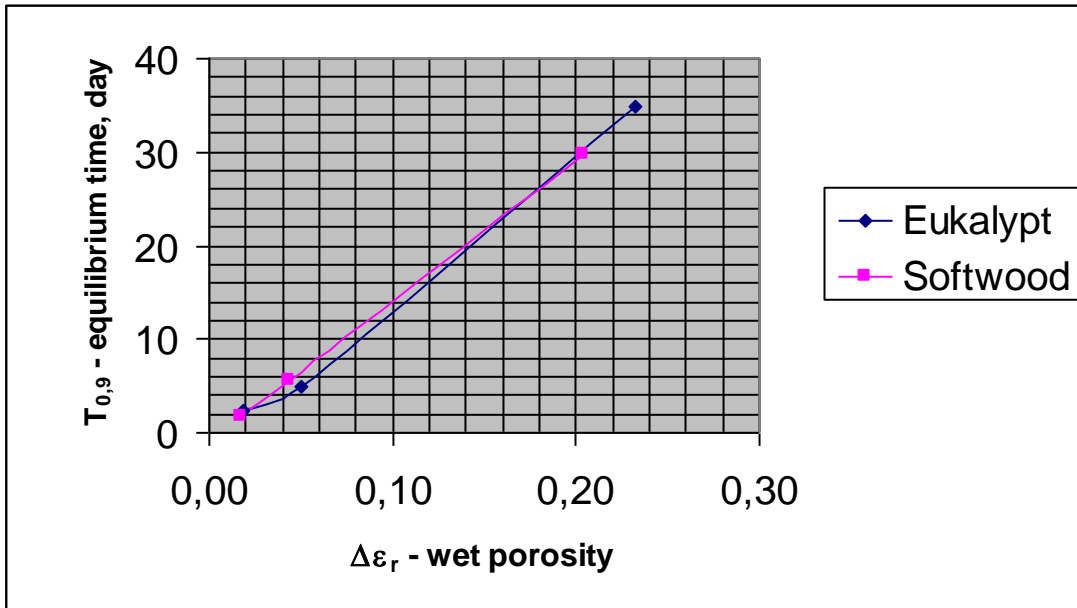


Fig. 6: Mean pore interval, ($r_\Delta - r_{min}$), vs. rel. pore concentration, z , filled with water

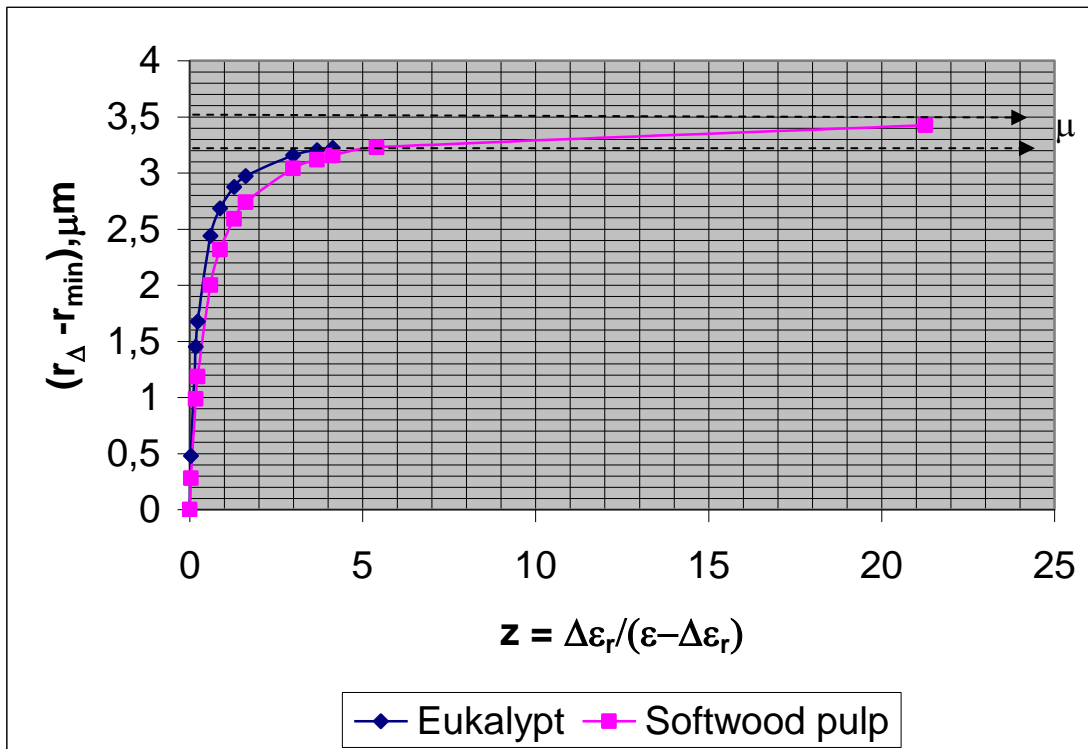


Fig. 7: Equilibrium moisture of pulp sheet vs. R.H.

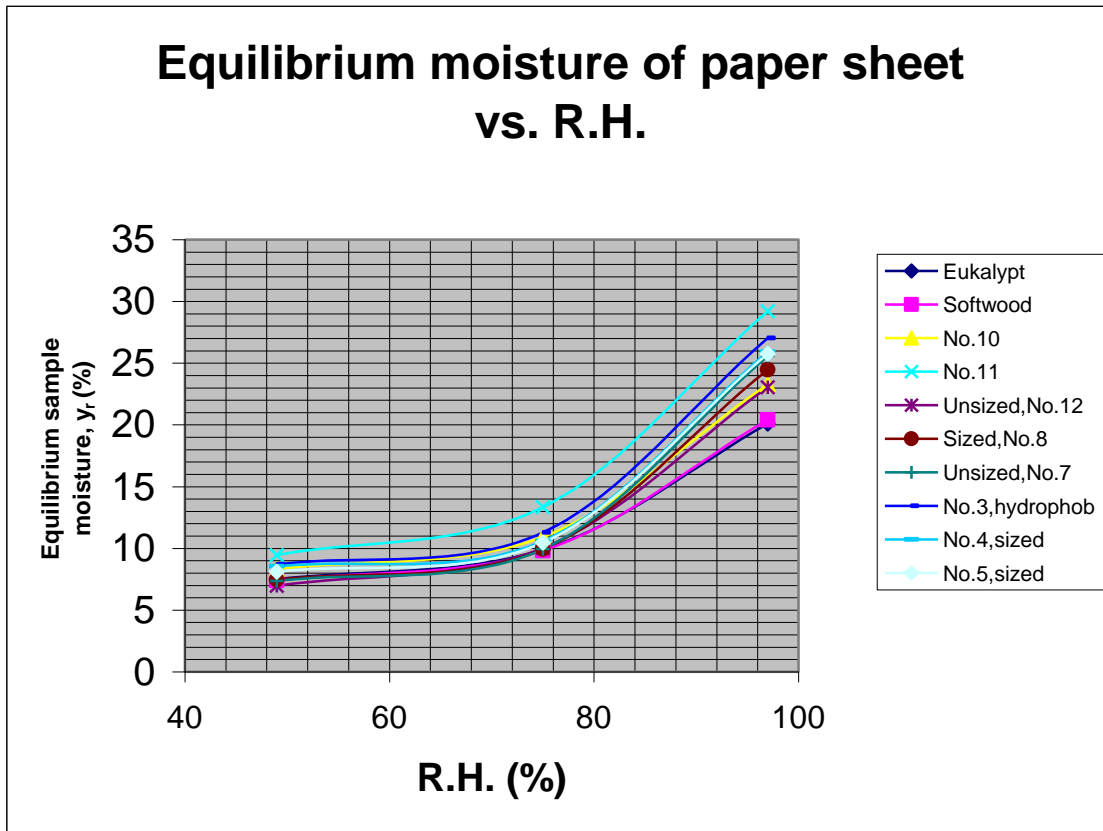


Fig. 8: Equilibrium moisture of paper sheet vs. its partial density

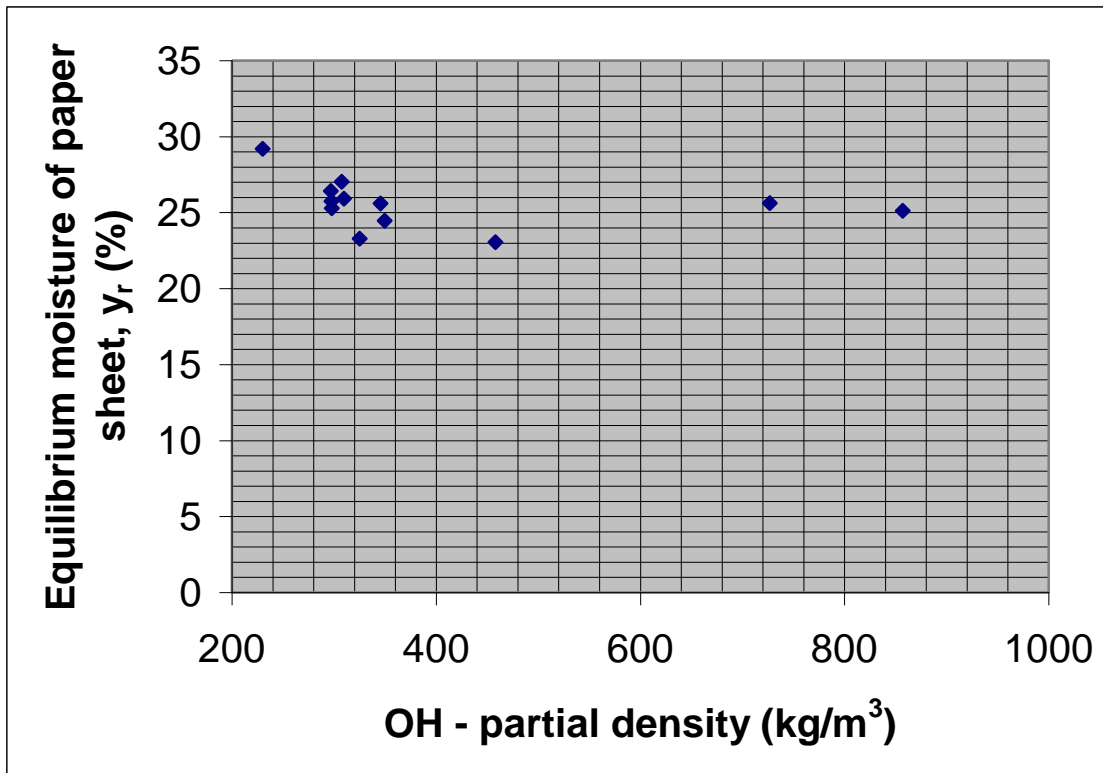
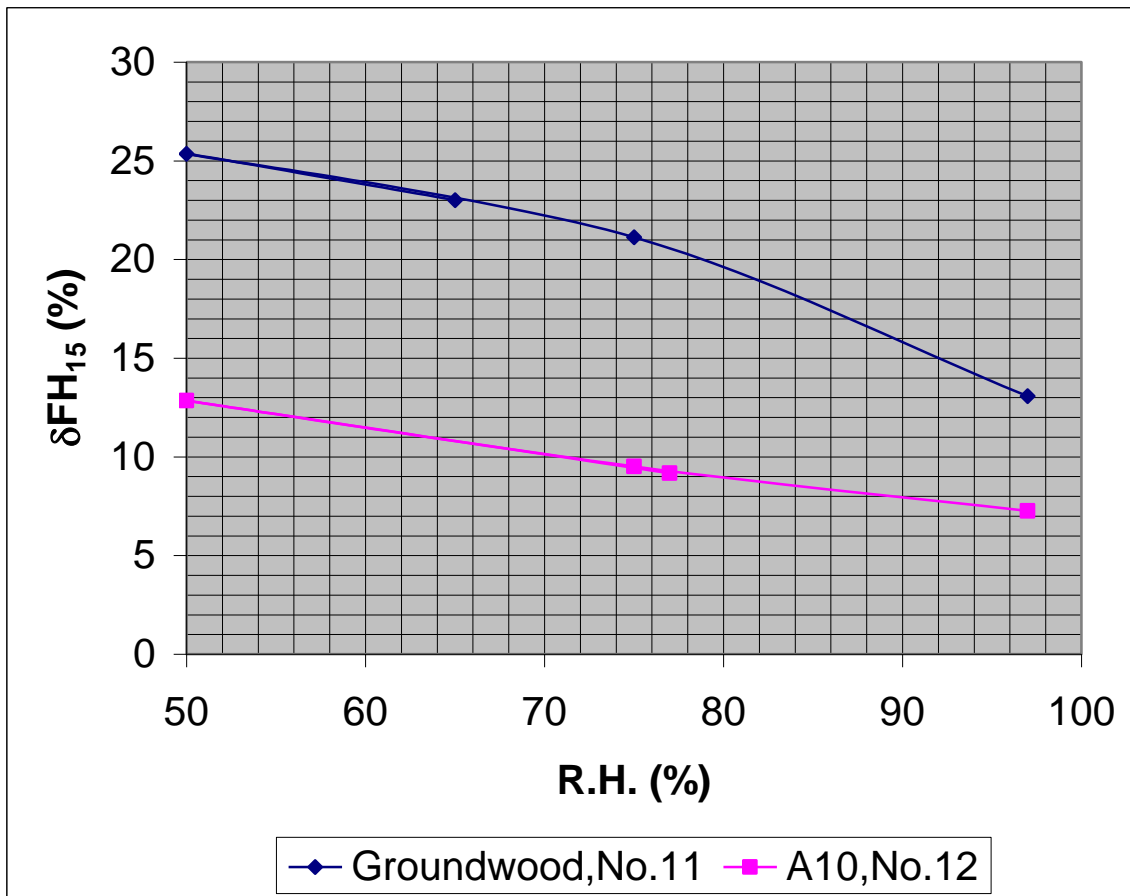


Fig. 9: Paper sheet-yielding vs. R.H.



List of symbols and parameters

AKD – sizing agent on alkyl ketene basis;

y - increment of sample moisture (w/w); $\mathbf{y} = \mathbf{y}_s - \mathbf{y}_0$, y_s - real moisture, y_0 – moisture of sample at start of experiment;

x - time (in days) of sample storage at given R.H.;

d - characterises the rate of steady state adjustment;

c - characterises a hygroscopicity of porous materials;

T_{0,9} and **T_{0,99}** - time needed to achievement 90% or 99% of steady state moisture of paper mass sample /day/;

$\mathbf{y}_r = \mathbf{c} + \mathbf{y}_0$ - steady state moisture of paper matter (rel. amount of water in porous paper medium w/w or %);

$\mathbf{v}_h^0 = \mathbf{c}/(\mathbf{1} + \mathbf{b})$ - humidity rate at the start of humidification of pore sample /day⁻¹/;

ρ_v - density of water (g/cm³);

OH - partial density of paper mass expressed by relation basic weight of paper sample divided by thickness of sample (g/cm³);

ρ_p - density of solid part of cellulosic material³ = 1,56 g/cm³;

ϕ_{rel} - relative humidity (R.H.) of air;

M - molecular weight of water = 18;

T - temperature (K);

θ - contact angle between surface of capillary tube and meniscus of water inside characterises its shape - (in the case of full wetting is usually this angle equal to 0° and expression ($\gamma_{l,g} * \cos \theta$) is equal to surface tension of water $\gamma_{l,g}$ (72,2.10⁻³ N/m at **T** = 295 K);

R - gas constancy (8,314 J.K⁻¹.mol⁻¹);

r(φ_{rel}) - radius of equivalent cylindrical pore (m);

r_{min} - radius of maximal equivalent cylindrical pore being occupied by condensed water at start of humidification process (μm);

A - outer surface of pore sample given by its geometry (m²);

A_f - free outer surface of pore sample (m²); **A_f** = **A** · **ε**;

ε - all porosity of pore sample (V/V); **ε** = **1 - OH/ρ_p** (e.g. see Skalický³);

ρ_l - liquid density, i.e. water density, **ρ_v** (g/cm³).

p - outer pressure on liquid within pore tubes (Pa);

p_r - partial pressure of the liquid contained in pores with equivalent pore radius of cylindrical pore (**r**; **r+dr**) (Pa);

p_∞ - partial pressure upon non-curved meniscus with **θ** = 0° ;

Π_{g-c} - geometrical and concentration factor of porous material in Eq. /8/;

Π_{s-m} - surface-molecular factor of porous material in Eq. /8/;

Π_{str} - structural factor characterizes pore structure of porous material in Eq. /8/;

σ_T - adhesion tension (mN/m);

$\gamma_{l,g}$ – surface tension of liquid, i.e. water at **T** = 294 K, $\gamma_{l,g}$ = 72.1 mN/m;

Δε_r – interval of pores (**r_{min}** ≤ **r** ≤ **r(φ_{rel})**), filled at steady state by condensed water at given environment condition, i.e. R.H. = **φ_{rel}**;

ε_r - interval of pores (**0** ≤ **r** ≤ **r(φ_{rel})**), filled in steady state by condensed water at given environment condition, i.e. R.H. = **φ_{rel}**;

μ - radius of equivalent mean pore radius from all pore interval ($0 \leq r \leq r_{\text{maxim}}$), μm ;
 r_r - radius of equivalent mean pore radius from pore interval ($0 \leq r \leq r(\varphi_{\text{rel}})$), μm ;
 r_{Δ} - radius of equivalent mean pore radius from pore interval ($r_{\text{min}} \leq r \leq r(\varphi_{\text{rel}})$), μm ;
 z - relative pore concentration (V/V) filled with water, i.e. a volume ratio of pores filled with water at R.H. = φ_{rel} to volume of free pores, $z = \Delta\varepsilon_r / (\varepsilon - \Delta\varepsilon_r)$;
 ω - compactness, i.e. negligible amount of biggest pores in porous sample and connectivity of numerical - represented by distribution $\mathbf{F}(\mathbf{r})$ or probability function $\mathbf{f}(\mathbf{r})$ - and volume - represented by distribution $\varepsilon(\mathbf{r})$ or probability function $\varepsilon'(\mathbf{r})$ - pore distribution of real porous material;
 k_h - proportionality coefficient of general character in Eq. /14/ ($\mu\text{m}^2 \cdot \text{m}^{-1} \cdot \text{mN}^{-1} \cdot \text{day}^{-1}$);
 $(\varepsilon_{97} - \varepsilon_{49})/\varepsilon$ or $(\varepsilon_{97} - \varepsilon_{75})/\varepsilon$ - extent of pore volume dispersion in porous material;
 b_{50} - median pore diameter measured by pneumatical permeation method (μm);
 $\Delta b = b_{90} - b_{10}$ - dispersity of pore distribution by pore difference parameter (μm);
 \mathbf{RbH} - bending strength (N/mm^2);
 \mathbf{FH} - supreme force (N);
 \mathbf{I}_p - deflection work (J);
 \mathbf{T} - stiffness of paper strip (N.mm);
 \mathbf{T}_0 - Stiffness Index of paper strip (N.mm);
 L_v - distance between support point (see Scheme 1), mm;
 δ - deflection in linear part of a relationship $F=f(\text{deflection})$, mm;
 b - width of specimen, mm;
 τ - thickness of specimen, mm;
 E - Young's modulus, calculated for every measured thickness of specimen by help of equation /16/ (N/mm^2);
 F - bending strength (see Scheme 1) corresponding deflection δ in linear part of a relationship $F = f(\text{deflection})$, N;
 I - moment of inertia the cross-section of measured specimen with a width b and thickness τ (mm^4);

Paper sheet-yielding parameters:

\mathbf{FH}_x - touch force to sample at its deflection x mm (N);
 \mathbf{dFH}_x - difference between the supreme force \mathbf{FH} and \mathbf{FH}_x (N);
 $\mathbf{\delta FH}_x$ - rel. difference $100 \cdot (\mathbf{FH} - \mathbf{FH}_x) / \mathbf{FH}$ (%).

Constancies in kinetic of humidification equation /1/: \mathbf{a} , \mathbf{b} , \mathbf{c} , \mathbf{d} ;

Constancies in /14/:

$$\mathbf{a}_h = \varepsilon \cdot \sqrt{\mathbf{K}}; \quad \mathbf{K} = k_h \cdot 4A \cdot (\gamma_{l,g} \cdot \cos\theta) \cdot (\rho_l / \text{OH})$$

$$\mathbf{b}_h = (\omega - 1) \cdot \sqrt{\mathbf{K}}$$

$$\mathbf{c}_h = r_{\text{min}} \cdot \varepsilon$$

$$\mathbf{d}_h = (\mu + r_{\text{min}}) \cdot \omega - r_{\text{min}}$$